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NEW THERMODYNAMICS: WHAT IS THERMAL ENERGY AND ITS DENSITY VERSUS HEAT CAPACITY

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Abstract

Traditional thermodynamics explains what is witnessed when heating matter, at both low and high temperatures, in terms of changes in heat capacities. To enhance our understanding, what constitutes thermal energy will be analyzed. It will then be demonstrated that it is actually the relationship between thermal energy density and temperature that changes, thus allowing heat capacities to theoretically remain constants.

Keywords

Heat Capacity, Thermal Energy Density, Blackbody Radiation, Cut-Off Wavelength

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1. Introduction

For: 400 K > T > 250 K, condensed matter has a heat capacity (C_v) that can be approximated by:

$$C_{v-solid} \approx C_{v-liquid} \approx 3R = 24.93 \text{ J/(K mole)} \quad (1)$$

Where the subscript "v" signifies the process being isometric (A.K.A. isochoric: dV=0) and "R" is the ideal gas constant: R = 8.31 J/mole.

Although not as clear in Fig. 1, for: 400 K > T > 250 K, a monatomic gas has an isometric heat capacity that can be approximated by:

$$C_{v-gas} \approx 3R/2 = 12.46 \text{ J/(K mole)} \quad (2)$$

Similarly, for: 400 K > T > 250 K, a polyatomic gas has its isometric heat capacity approximated by:

$$C_{v-gas} = R(n" + 1/2) \quad (3)$$

where "n"" represents the number of atoms in a gaseous molecule. Note that eq. 2 and 3 have been explained in terms of this author's improved kinetic theory [2]-[4].

When an isobaric system expands, it performs lost work onto/into the surrounding atmosphere, as defined by:

$$W_{lost} = (PdV)_{atm} = nRdT \quad (4)$$

Lost work [$(PdV)_{atm}$] has been described by this author as the energy that is expended by an expanding system when lifting the overlying atmosphere's mass. Ultimately, it signifies an atmospheric potential energy increase [4]-[9].

Therefore, for: 400 K > T > 250 K , an expanding monatomic gas has an isobaric (dP=0) heat capacity that can be approximated by [4],[5]:

$$C_{p-gas} = C_{v-gas} + R = 5R/2 = 20.78 \text{ J/(K mole)} \quad (5)$$

where the subscript "p" signifies the process as being isobaric (dP=0).

Similarly, for: 400 K > T > 250 K, a polyatomic gas has an isobaric heat capacity that can be approximated by [2]-[4]:

$$C_{p-gas} = R(n" + 1/2) + R = R(n" + 3/2) \quad (6)$$

Equations 1, 2, 3, 5 and 6 are all valid approximations. They are focused upon the molecule's motions. They do not fully consider all the EM components in either gases or condensed matter. Furthermore, equations 2,3, 5 and 6 do not take into account any energy associated with any photons residing in the freespace surrounding the gas molecules.

Furthermore, eq. 1 is isometric. If the condensed matter expands in some isobaric process then one should consider any work done in lifting the atmosphere, as defined by:

$$W_{lost} = (PdV)_{atm} \quad (7)$$

As illustrated in Fig. 1, a solid's heat capacity asymptotically approaches zero, as the solid's temperature approaches absolute zero ($T \rightarrow 0$).

The accepted theory for heat capacities when approaching absolute zero has a certain basis in statistical thermodynamics. A theory that originates in the late 19th/early 20th century from the likes of Maxwell and Boltzmann. This theory is also partially founded in Einstein's (1907) photoelectron model which is based upon a 3-d crystalline solid possessing a large number of quantum harmonic oscillators. Einstein's theory qualitatively explained the heat capacities as $T \rightarrow 0$, but quantitatively there are problems with the analysis. This seemingly was resolved with Debye's analysis.[1]

Debye (1912) extended Einstein's theory with the solid-state equivalent of Planck's law for blackbody radiation, which treated EM radiation as a

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[1] As a side note, Einstein's theory can be taken as one of the early quantum-founded analysis. Interesting, Einstein, Podosky and Rosen (EPR argument) eventually argued that quantum theory is an incomplete theory [10]. Although quantum theory is currently embraced by the majority, some still argue that there are unresolved issues. One issue being that energy releasing processes tend to be irreversible, while quantum is limited to reversible phenomena [11]. Einstein further noted that quantum mechanics can only represent point-like particles in a vacuum. Of interest, this author's understandings of lost work, limits reversibility of expanding systems to vacuums [4], something that entropy-based traditional thermodynamics fails to elucidate, i.e., work must be done onto something e.g., lifting of the overlying atmosphere's mass against Earth's gravity by an expanding system [4]-[9].

photon gas confined in a vacuum space. Debye T^3 law arrived is accepted as being a superior fit to experimental findings.

Debye's T^3 law considers that the isometric heat capacity at low temperatures, varies as the cube of temperature, e.g.,:

$$C_{v-solid} = A"(T/\theta)^3) = AT^3 \quad (8)$$

where "A" " and "A" are constants and θ is the Debye temperature.

Furthermore, for an ideal gas, the accepted theory for molar heat capacities of gases is based upon the degrees of freedom (f) analysis, i.e.:

$$C_v = \left(\frac{f}{2}\right) R \quad (9)$$

and

$$C_p = C_v + R = \left(\frac{f}{2}\right) R + R \quad (10)$$

Degrees of freedom arguments are founded upon equipartition where a gas molecule has a mean energy of: $kT/2$ per degree of freedom, with "k" being Boltzmann's constant. Such degree of freedom arguments should be questioned because they assert that a gas molecule automatically obtains a mean energy ($kT/2$) per degree, without any clarity explaining the energy's origins.

Furthermore, traditionally one relies upon quantum arguments, e.g., cooling molecules move from a higher to a lower quantized energy state. Moreover, the fraction of molecules in the lowest energy state approaches unity, as the temperature approaches absolute zero. Such arguments have their place when contemplating the excitations of electrons but thermal energy may be better contemplated in terms of broad continuous spectrums of energy rather than discrete/quantized energy states.

A goal of this paper is to explain what has been witnessed without relying upon Einstein's analysis, or Debye's T^3 Law. A result will be an improved understanding concerning what constitutes thermal energy. A result that does not rely upon discrete quantized states.

2. The Essentials For: 400 K > T > 250 K

Eq. 1 can be employed to approximate the thermal energy (Q_{in}) required to raise the temperature of n moles of condensed matter by dT:

$$Q_{in-v} = 3nRdT = nC_{v-solid}dT = nC_{v-liquid}dT \quad (11)$$

For the isometric heating of n moles of a monatomic gas, eq. 2 can be used to approximate the thermal energy (Q_{in}) required to raise the gas' temperature by dT:

$$Q_{in-v} = \left(\frac{3}{2}\right) nRdT = nC_{v-gas}dT \qquad (12)$$

Similarly, for the isometric heating of n moles of a polyatomic gas, eq. 3 can be used to approximate the thermal energy (Q_{in}) required to raise the gas' temperature by dT:

$$Q_{in-v} = (n" + 1/2)nRdT = nC_{v-gas}dT \qquad (13)$$

And, for the isobaric heating of n moles of an expanding monatomic gas, eq. 5 can be used to approximate the thermal energy (Q_{in}) required to raise the gas' temperature by dT:

$$Q_{in-v} = (n" + 3/2)nRdT = nC_{v-gas}dT \qquad (14)$$

Similarly, for the isobaric heating of n moles of a polyatomic gas eq. 6 can be used to approximate the thermal energy (Q_{in}) required to raise the gas' temperature by dT:

$$Q_{in-p} = \left(\frac{3}{2}\right)(n" + 3/2)nRdT = nC_{p-gas}dT \qquad (15)$$

For: $T < 250$ K. Conversely, for the heating of n moles of condensed matter, eq. 8 can be used to approximate the thermal energy (Q_{in}) required to raise the temperature by dT:

$$Q_{in-v} = AT^3dT = C_{v-solid}dT \qquad (16)$$

Equations 1 through 6, eq. 8, and equations 11 through 16, all assume that the heat capacities are constants and that the thermal energy is some linear increasing function of temperature, i.e., for $T > 250$ K:

$$dT = T_f - T_i \qquad (17)$$

where the subscripts "f" and "i" respectively signify the final and initial states.

3. The Essentials For: $T < 250$ K

For: $T < 250$ K, one can integrate eq. 16 (based upon Debye's T^3 law), thus obtaining for condensed matter:

$$Q_{in-v} = \int dq_{in-v} = A\int_{T_i}^{T_f} T^3dT = (A/4)(T_f^4 - T_i^4) \qquad (18)$$

Generally condensed matter can be contemplated as being isometric. Therefore, one can contemplate eq. 18 in terms of energy density, thus:

$$Q_{in-v}/V = (A/4V)(T_f^4 - T_i^4) \quad (19)$$

Are there any relations in thermodynamics that are a function of T^4? What comes to mind is the Stefan-Boltzmann's equation for a blackbody radiation spectrum:

$$\rho_B = \sigma T^4 \quad (20)$$

where "ρ_B" is the blackbody radiance (energy density), and "σ" is the blackbody radiation constant: $\sigma = 8\pi^5 k^4/15c^3h^3$ = 5.670374419...$\times 10^{-8}$ (W·m^{-2}·K^{-4}).

The constants in eq. 19 and eq. 20 are not one and the same, i.e., $a \neq (\frac{A}{4V})$. However, the blackbody energy flux as described by eq. 20 is founded upon the thermal energy emitted by certain closed system's walls, into that closed system's freespace.

4. The Essentials, For All T

Certainly, all condensed matter above absolute zero emits energy whose broad continuous spectrum often approximates a blackbody spectrum. This radiated thermal energy is a part of what can be referred to as radiant energy. Radiant energy can take many forms ranging from gamma rays to microwaves. The question then becomes, what part of the spectrum is related to thermal energy in condensed matter?

In order to answer that question, one starts by considering the energy density $[u(v,T)]$ associated with blackbody radiation in a closed system. As defined by Planck's formula:

$$u(v,T) = \left(\frac{8\pi h}{c^3}\right) v^n / e^{(\frac{hv}{kT}-1)} \quad (21)$$

The wavelength version of eq. 21, for the energy density of a blackbody spectrum between λ and $d\lambda$ is the energy per mode: ($E = \frac{hc}{\lambda} = hv$), times the density of states per photon, times the probability that the mode is occupied. That being:

$$u(\lambda)d\lambda = \left(\frac{8\pi hc}{\lambda^5}\right)\left[\frac{1}{e^{\left(\frac{hv}{kT}-1\right)}}\right]d\lambda \quad (22)$$

Plank's eq. 22 is useful for calculating the total energy density (J/m^3)

associated with a full blackbody spectrum in an enclosed freespace. Based upon eq. 22, plotting the total energy density, one obtains Fig. 2.

Let's reconsider condensed matter. From an energy density perspective condensed matter concentrates thermal energy, when compared to the surrounding radiation density in freespace. It is inarguable that when considering a vacuum in thermal equilibrium that the vacuum's walls must absorb as much thermal energy as they emit.

The exact mechanism for the emittance and absorption of thermal spectrum lacks any clarity. Interestingly, this author has previously proposed that such thermal spectrum is due to inelastic collisions (both intermolecular and intramolecular). Furthermore, a plausible explanation concerning the mechanism that creates the thermal photons associated with radiated thermal energy may be the physical distortions of the electron clouds within molecules and/or atoms, during inelastic collisions [4], [12].

Thermal photons are considered to belong to a broad continuous EM spectrum. The part of the EM spectrum of energy that tends to be both absorbed and emitted by matter.

Whatever the mechanism turns out to be, it must explain why thermal spectrums are:

1) Universal to all condensed matter above absolute zero.
2) Have a temperature functionality.
3) Disappears as: $T \rightarrow 0\ K$

Interestingly, the above 1), 2) and 3) also applies to the thermal energy density within matter. However, the temperature functionality for matter energy density is approximately linear, at least for: 450 K > T > 250 K. Conversely, a blackbody's energy density clearly is not linear, as is illustrated in Fig. 2

Strangely, for T < 250 K, based upon Deby's energy density (eq. 19), one would get a graph similar to that depicted in Fig. 2

As previously stated the above has traditionally been reconciled by contemplating that heat capacities are temperature dependent, rather than constant through all temperature regimes.

5. New Graphical Analysis

The problem with eq. 22 (hence, Fig. 2) is that it considers all wavelengths of a blackbody spectrum. Thermal energy only concerns the

wavelengths (frequencies) that tend to be absorbed by matter, thus becoming thermal energy within that matter. It is accepted (without absolute clarity) that wavelengths associated with thermal energy predominately resides in the infrared part of the spectrum. Therefore, contemplating the total energy density (full spectrum), as sketched in Fig. 2, can be disingenuous.

Accepting that thermal energy consists of only part of the total energy density. Then in order to calculate the thermal energy density, one only needs to consider the part of the spectrum that is predominately thermal energy. What parts of the EM spectrum does one quantify as being thermal energy?

The thermal spectrum resides in the infrared: $0.75\ \mu m = 750nm < \lambda < 100\ \mu m = 100{,}000\ nm$ However, the division between visible light and infrared is founded upon our human vision rather than any concise notions of thermal energy. Accordingly, this analysis depends upon where one chooses to start their consideration of what constitutes thermal energy.

In remote sensing (often used by geologists) the thermal spectrum is considered to be in the range of: $3\ \mu m < \lambda < 15\ \mu m$. In thermodynamics the thermal infrared is considered to be in the range of: $8\ \mu m < \lambda < 15\ \mu m$. The difference can be attributed to the fact that remote sensing sometimes involves spotting forest fires whose emitted wavelengths are close to 3 μm. Again, there is no universal understanding concerning thermal energy.

Based upon Fig. 1, one can speculate that the transition between linear and T^3 functionality for the energy density within condensed matter, occurs near 250 K. Thus, one begins the analysis by examining the energy density for: $T = 250$ K, as illustrated in Fig. 3. One immediately notices that the peak is near $11.4\ \mu m$. Consider that the thermal energy starts somewhere in the range: $8\ \mu m < \lambda < 12\ \mu m$.

Unfortunately, the integration (of eq. 21 and/or eq. 22) can only be performed over all wavelengths ($0 < \lambda < \infty$) (this is accomplished using mathematical tricks). Therefore, one cannot simply calculate the thermal energy density associated with only some part of a blackbody spectrum. However, one can graphically approximate the thermal energy density associated with various parts of the blackbody spectrum.

One starts by sketching and graphically calculating the total energy density for all temperatures between 50 K and 600 K degrees. This was done at 25 K intervals using graphs obtained from a website that provides the "Planck Curve for Blackbody Radiation", as was published by TU Graz University of Technology [13].

The total energy density of blackbody radiation was obtained using geometric approximations. For example, adding the areas of triangles A, B and C plus the rectangle D, as illustrated in Fig 4 for four different temperatures. The result for the total thermal energy was plotted in Fig. 2.

A similar graphical technique was then used to calculate what is then to be considered as the "thermal energy density". A cut-off wavelength (λ_{cut}) between what is considered thermal energy and non-thermal energy was determined.

Three cut-off wavelengths were chosen: $\lambda_{cut} = 8\,\mu m$, $\lambda_{cut} = 10\,\mu m$ and $\lambda_{cut} = 12\,\mu m$. Fig. 5, illustrates the thermal energy density at four different temperatures (100, 200, 300 & 400 K), for $\lambda_{cut} = 10\,\mu m$, hence over the range: $10\mu m < \lambda < \infty$.

The data table for total energy density and thermal energy density, as well as the energy flux (based upon the Stefan-Boltzmann equation: eq. 20) is given in Table 1, at the end of the paper.

Plotting the total energy density, and the total thermal energy density versus temperature for the three cut-off wavelengths (λ_{cut}), one obtains Fig. 6. It is of interest that the total thermal energy density can be approximated as a linear relation for: 250 K < T < 400 K. The approximate slopes for the thermal energy density using the three cut-off wavelengths are:

$\lambda_{cut} = 8\,\mu m$: (12.58-2.59/ (400-250) = 6.6 x 10^{-2} J/m^3/K
$\lambda_{cut} = 10$ µm: (9.45 -2.27)/(400-250) = 4.8 x 10^{-2} J/m^3/K
$\lambda_{cut} = 12$ µm : (6.99 – 1.95)/(400-250) = 3.4 x 10^{-2} J/m^3/K

It must be emphasized that this analysis was formulated to show that, if the thermal energy density had a thermal energy cut-off wavelength, then one may be able to explain why thermal relationships are approximated as being linear functions of temperature for: 250 K < T < 400 K.

Furthermore, for: T < 250 K the thermal energy density would be a rapidly decreasing function of temperature. Thus, it becomes likely that the heat capacity approximates being a constant through all temperatures.

Moreover, it is the thermal density that is not a linear function of temperature over all temperature regimes.

It becomes a case of our residing on Earth's surface, that we have intuitively come to falsely believe that thermal energy is a linear function of temperature.

In accepting this analysis, one assumes that the thermal energy density associated with matter's thermal spectrum, can be related to the thermal energy density within condensed matter. Based upon the fact that they are both linear relations of temperature, one must conclude that such a relationship may exist. Unfortunately, at this point this relationship is not fully realized. Of interest, one should include the fact that the thermal spectrums emitted by condensed matter, tend to resemble cut-off blackbody spectrums.

Furthermore, the thermal energy cut-off at: 8 μm, 10 μm, and 12 μm, were somewhat arbitrarily made. Certainly, a superior cutoff may be obtained by performing a more exacting analysis over a broader range of wavelengths and by considering various types of condensed matter. Note that this author also tried a cutoff of 3 μm with a preliminary determination that it was too low (see the next section: Weakness of Graphical Analysis).

Moreover, the cut-offs were chosen to be vertical and linear, when in fact it may vary and actually be dependent upon the nature of the condensed matter itself. Even so, there should be a certain degree of universality.

A point becomes that one does not necessarily have to rely upon Einstein's quantum arguments and/or Debye's T^3 law to explain why the total energy required to heat matter has temperature dependence. Again, the simpler explanation may ultimately reside with the realization that it is the thermal energy density that changes with temperature rather than the heat capacity varying in different temperature regimes.

6. A Weakness in this Graphical Analysis

Looking at Fig. 5 one will notice that as the temperature increases, the cut-off wavelength of interest shifts right with increasing temperature. The reason that this analysis was stopped at T = 500 K is that the cut-off wavelength approached C in Fig. 5. At which point, this graphical analysis becomes increasingly inaccurate (see the data points with ** in Table 1).

The expectation should be that as the temperature increases, the thermal energy density continually increases, which is not necessarily what one gets

when doing simple time- consuming geometric analysis, as was done herein. It would be of interest for someone to extrapolate this analysis, perhaps using computing, e.g., artificial intelligence (AI).

7. What does the Cut-Off Represent?

Whether it is ultimately placed at 8 μm, 10 μm, 12 μm, or some other value, the cut-off wavelength (λ_{cut}) represents a theoretical limit for the thermal energy, that being the energy associated with the kinematics within matter. A result of such kinematics is energy radiating from all condensed matter that is above absolute zero. With kinematic energy being the kinetic (translational plus rotational) plus vibrational energy in matter. This statement is partially based upon this author's kinetic theory [2]-[4] wherein the separation of these energies differs from the traditionally accepted degrees of freedom, based theorization.

As stated, there are various types of radiant energy. These include microwave, visible light, ultraviolet, x-rays and gamma rays. What needs to be added to this list is thermal energy, which should be placed between the microwave and visible light spectrums. Herein, the proposal being that thermal energy now starts at the cut-off wavelength and extends into longer wavelengths, e.g., the far infrared, and perhaps even into the microwave.

Again, for condensed matter, thermal energy includes the energy spectrum associated with the vibrational energies inside that matter. It represents the wavelengths/frequencies of energy that are radiated and (most likely) absorbed by that matter.

Importantly, thermal energy is not limited to the discrete energies that are readily absorbed and radiated by electrons, i.e., the quantized energies often determined in infrared spectroscopy. When contemplating closed systems, thermal energy is the energy that is both radiated and absorbed by the walls, which often can be blackbody in nature.

Thermal energy is a broad continuous spectrum of energy. Is it plausible that such a broad spectrum is somehow absorbed by the atoms and/or molecules, as a whole? That would certainly help one to understand why thermal equations involve both the number of molecules and/or the number of atoms.

A possible implication being that this energy is absorbed by nuclei and/or their components. This plausibility has previously been briefly pointed out by this author [4], [12]. Whatever the exact mechanism for the absorption and emission of thermal energy, its result is the vibrational energy within

condensed matter. Importantly, since the heat capacities are based upon the number of atoms in molecules, there must be some sort of approximate universality. A universality not readily explained by either the configuration of its electrons, or the shapes of their electron clouds.

8. Gases

Can any of the above be applied to gases?

For monatomic gases the heat capacities have been deemed to be relatively constant. However, that is not the case for polyatomic gases over all temperature regimes.

Fig. 7 shows the isometric specific heat of air (99%: O_2 and N_2) over a broad temperature range: $0 < T < 2000$ K. Note that engineers prefer to use specific heat which is related to the gas's mass. Physicists and chemists prefer to use molar heat capacities, which are related to the number of moles of gas.

As shown in Fig. 7, for, $T < 200$ K, a polyatomic gas' isometric specific heat [heat capacity per unit mass (c_v)] has been deemed to be some rapidly increasing functions of decreasing temperature, e.g., as: $T \rightarrow 0\ K$.

Furthermore for, 200 K $< T <$ 375 K, a polyatomic gas' isometric specific heat (c_v) has been considered to approximately be constant, as described by eq. 3.

Furthermore, for, 375 K $< T <$ 1750 K, a polyatomic gas' isometric specific (c_v) has been considered as being a linear increasing function of temperature.

Note that Fig. 7 extends to 2000 K, while the analysis for solids stopped at 500 K. This was due to the previously stated weakness in this graphical analysis.

Interestingly, the fact that monatomic gases have a relatively constant heat capacity as defined by eq. 2, implies that not all gases behave the same. Seemingly, gases that have vibrational energy as part of their total thermal energy are the only gas's whose heat capacities have temperature dependence. That being the case, then the kinetic energy (translational plus rotational) [2]-[4] is not affected, at least in the same way that vibrational energy is.

Is there anything that confirms the above? An indirect proof resides with the density of gases being a function of temperature. Specifically, the mean

molecular volume of a gas should be related to its mean kinetic energy: $3kT/2$. Ditto, a gas' mean molar volume is related to its mean molar kinetic energy: $3RT/2$. In other words, as the gas' temperature increases its kinetic energy increases. Therefore, the gas' mean molecular volume should increase.

Conversely, as the gas' temperature decreases the number of moles of a gas per unit volume (m^3) should increase. As shown in Fig. 8, the number of moles of a gas per unit volume, increases linearly as the temperature decreases from 320 K to 160 K. As the temperature decreases below 160 K, i.e., $T \rightarrow 0\ K$, the number of moles per cubic meter increases rapidly.

The above is expected. That is if the gas' thermal energy density decreases rapidly as: $T \rightarrow 0\ K$. Perhaps, what was not expected is this. As shown in Fig. 8, this equally applies to both monatomic and diatomic gases, namely hydrogen (H_2), helium (He), nitrogen (N_2), argon (Ar) and oxygen (O_2). The implication being that both monatomic and diatomic gases witness the same degradation of kinetic energy, as: $T \rightarrow 0\ K$.

An explanation for the similar degradation of kinetic energy is as follows. This author's kinetic theory implies that the larger structured wall molecules impose their kinematics upon the smaller gas molecules [2]-[4]. This means that both the monatomic and diatomic gases will obtain the same mean kinetic energy from their collisions with the structured vibrating wall molecules, as is defined by: $3kT/2$.

The overall implication is that it is the changes to a polyatomic gas's absorption of vibrational energy that separates the energetics of polyatomic gases from monatomic gases, as: $T \rightarrow 0\ K$.

9. Thermal Energy Density of High T Gases

For a diatomic gas (e.g., 99% of air), eq. 3 can be used to approximate the isometric heat capacity: $C_{v-gas} \approx 5R/2$, which it clearly is for: $T = 250$ K (see, Fig. 7) and remains approximately so for: 250 K $< T <$ 375 K. Unexpected is that its heat capacity then increases with temperature. It approaches the theoretical isobaric heat capacity for a diatomic gas, as defined by eq. 8. That being $C_{p-gas} \approx 7R/2$ at high temperatures (blast furnace temperatures, e.g.: 1,500 K)

How does one explain the seemingly heat capacity's increase for: 375 K $< T <$ 1750 K, shown in Fig. 7? Consider the heat capacity to be constant,

then again, it is the required thermal energy in per degree temperature change that increases. In other words, $Q_{in\text{-}v}$ as defined in eq. 13 increases because there is an unexpected increase to the thermal energy density in relation to the gas's temperature increase. Obviously, the gas' thermal energy density increase is greater than eq. 13 implies, as illustrated in Fig. 7 for: $T > 375$ K.

An implication of Fig. 7 is that the thermal energy density of the surrounding thermal (or blackbody) radiation increases rather rapidly between: 450 K< T < 750 K. After which, the increase tapers off: 750 K < T < 1750 K. Seemingly approaching some linear increasing value as temperatures exceed 2000 K. It would be of interest to attain a superior analysis of the thermal energy density at higher temperatures than has been provided by the graphical analysis herein. Again, hopefully such an analysis may be improved, e.g., by using AI computing.

10. Thermal Energy Density of Low *T* Gases

The traditional explanation for the heat capacity of a gas increasing as temperatures approach absolute zero, (i.e. for: $T < 250$ K, as: $T \rightarrow 0$) was based upon the concept that states can be frozen-out. Specifically, the vibrational energy of gases (e.g., air), are increasingly frozen-out as the temperatures decrease. Perhaps, but air is 99% homonuclear O_2 and N_2, both of which traditionally speaking, are supposedly transparent to thermal radiation.

Imagine that O_2 and N_2 truly are transparent to thermal radiation/photons, as has been traditionally claimed. One, might then ask, what difference would being frozen-out make? One faces that enigma bestowed in 20th century thermodynamics. That being, energy does not simply exist, as is implied by equipartition and degrees of freedom, founded kinetic theory.

Energy associated with a gas molecule must have an origin. For the case of a diatomic gas molecule in a closed system, this author's kinetic theory's origins are [2]-[4]:

1) Kinetic energy (translational plus rotational) is primarily imposed onto the diatomic molecule through the gas molecule's collisions with structured vibrating wall molecules.
2) Vibrational energy is primary obtained from the absorption of thermal photons.

Additionally, if homonuclear diatomic gases (e.g., O_2 and N_2) actually

are transparent to all thermal radiation, then being frozen-out would have no consequences. In which case, the diatomic gas must obtain both its kinetic and vibrational energy from its collisions with walls. Based upon heat capacities, this seemingly is not the case [2]-[4].

Importantly, thermal energy consists of broad continuous spectrums of energy, e.g., blackbody spectrums. Again, this differentiates thermal energy from quantized energies associated with the discrete energy states that are associated with electrons. It raises the question, is there another plausible explanation?

The simplest explanation for what is witnessed for gases at low temperatures is that the thermal energy density rapidly approaches zero, as: $T \rightarrow 0\ K$. Thus, one has the illusion that the heat capacity has skyrocketed, when in fact it is thermal energy density that has crashed.

In terms of polyatomic gases (e.g., air: 99%: N_2 and O_2) any thermal energy absorption resulting in vibrational energy would rapidly approach zero as: $T \rightarrow 0\ K$. Hence, the vibrational energy of that gas would also rapidly approach zero.

One may prefer to think in terms of the gas' vibrational energy being frozen-out at low temperatures. In many ways both arguments have similar results. A point becomes that one is not restricted to quantum arguments in order to comprehend why air's heat capacity has the illusion of being some rapidly increasing function of temperature as: $T \rightarrow 0$.

Moreover, thermal energy concerns the motions and vibrations of atoms/molecules as wholes. The energy associated with such motions quickly becomes zero as: $T \rightarrow 0\ K$. This is not the same as the energy associated with electrons. It is one thing to say that molecular motions cease, however this does not imply that electrons necessarily stop moving.

11. O_2 and N_2 Are Not Completely Transparent

How can diatomic gases like O_2 and N_2 be transparent to thermal radiation, yet their heat capacities adhere to standardized equations 2, 3, 5 and/or 6?

Heat capacity experiments involve the measurements of thermal energy in (Q_{in}) versus the temperature change (dT). The required energy is based upon the gas's kinematics, i.e., the gas's kinetic plus vibrational energies. For all intents and purposes, thermal energy constitutes wavelengths that are greater than the cut-off wavelength. That being the previously described

theoretical division for thermal energy, i.e., the thermal part of the infrared spectrum.

The concept of certain gases being transparent is founded upon infrared spectroscopy, which often focuses upon shorter wavelengths photons (higher frequencies/energies). Those, being the photons that tend to interact (as waves) with various gases electron configurations, e.g., a gas' lopsided charge distribution. To what extent the absorption due to different electron configurations actually results in the heating of a gas, may become debatable on a case-by-case basis.

Many believe that the absorption of discrete wavelengths due to electron configurations is the primary mechanism by which gas molecules absorb thermal energy. In terms of this paper, so-called transparent gases likely absorb thermal photons. They do not absorb the higher energy (shorter wavelength) photons that tend to excite discrete energy states in gases like CO_2. Note that CO_2 also has a strong absorption peak near $15\ \mu m$.

It is of interest that in remote sensing, the wavelengths in the thermal part of the EM spectrum forms one of the windows for observing the Earth from satellites. Seemingly, the majority (up to 80%) of the photons in this window do readily pass through the atmosphere. An implication being that the absorption of thermal photons by gases is inconsequential.

Due to the speed of light, the absorption of thermal photons by gases can represent relevant quantities of thermal energy. Imagine a closed system where thermal photons are both radiated and absorbed by the walls. Certainly, the chances of a given photon scattering with and then being absorbed by a given gas molecule, remains low. However, the quantity of photons that can interact with that gas molecule over a given duration renders the absorption of thermal photons by gas molecules, real.

12. Infrared Spectroscopy

Would all of a gas' absorptions be witnessed in infrared spectroscopy? In dispersive infrared spectroscopy, the resulting sample's spectrum is obtained by subtracting a background (or zero) spectrum from one's measurements. The resultant spectrum then shows any uniqueness which often is based upon the sample gas's unique electron configuration, e.g., lopsided charge distributions. This uniqueness enables one to quickly identify the gas.

Consider that Fig. 9. Path 1 (reference cell path) will have the same interference (absorptions and radiances), as Path 2 (sample cell path). The

interference along Path 1 when measured gives the background spectrum. This interference comes from the air, contents of the reference cell, laboratory and/or apparatus etc. The subtraction of the background spectrum means that the recorded spectrum only shows uniqueness associated with the sample being tested. A uniqueness that is based upon discrete energy associated with specific wavelengths, which are amplified before the spectrum is recorded.

It should be emphasized that both the analyte cell (sample cell) and the reference cell are enclosures. The reference cell is either evacuated (vacuum) or is filled with a gas that is considered as being non-absorbing, e.g., air (99% homonuclear O_2 and N_2). As enclosures, both cells contain thermal (e.g., blackbody) radiation that is related to their temperature. Furthermore, the light source is a heated wire radiating a thermal (e.g., blackbody) spectrum that is associated with its higher temperature. Therefore, much of the subtracted background will constitute a broad continuous thermal (e.g., blackbody) spectrum, whose peak is in the vicinity of the previously described cut-off wavelengths, e.g., $\lambda_{cut} = 10\ \mu m$.

Few have asked, does the background subtraction have any consequences, other than enabling the identification of the gas? If the background spectrum includes some universal phenomenon, then the resulting spectrum becomes misleading from a thermal energy perspective. For example, if both the analyte and the reference gas absorbed (or emitted) the similar parts of the light source's spectrum. Then it becomes erroneous to assume that the parts of the subtracted background spectrum are in no way universal to all (or most all) gases. In which case, the background subtraction includes the subtraction of certain gas' thermal signature, or part thereof.

Similar argument holds for Fourier Transform Infrared Spectrometry (FTIR), where the background's subtraction occurs in its computer and programming. Note that in FTIR the background spectrum is often measured in the cell prior to testing the sample. Its data is stored in the computer, where the background spectrum is subtracted.

Interestingly, in inelastic collision studies, infrared spectroscopy is used. Furthermore, as previously stated most such studies are performed in ultracold experimental apparatus, hence certain aspects of the thermal spectrum would be eradicated.

The plausibility that some universal phenomena may not be witnessed in

the infrared spectroscopy, raises concerns that may help one's understanding.

13. Discussion

Nothing was proven here beyond all doubt. Ditto can be said for Einstein's photoelectron model which treats solids as a group of quantum oscillators. The same applies to Debye's T^3 law. Certainly, both Einstein's and Debye's models are based upon mathematical results. Results that can be tied to both statistical and quantum theory.

The issue with such results, is that one often places mathematics ahead of theoretical logic, i.e., one's pet theory is purely mathematical thus, leaving theoretical justification by the wayside. In this paper a theory was devised ahead of the math, a theory whose plausibility was verified using graphical analysis. A theory that fits with and clearly explains accepted thermodynamic relations.

It is interesting to note that both Stefan-Boltzmann's and Planck's energy density relations, are in many ways part of quantum theory's origins. Interestingly, this is the point that this theory separates from the traditional understandings. It raises questions, e.g., are such accepted relations founded upon mathematical tricks, or divine logic? Planck thought that the quantization of energy was a mathematical trick enabling one to advert the ultraviolet catastrophe [16]. Certainly, at that point Planck was thinking in terms of classical oscillators.

The issue is not with the quantization of a photon's energy, rather it is the notion that thermal energy is only adsorbed by electrons possessing discrete quantized energy states. The states that are found in infrared spectroscopy results, enabling one to identify specific gases. Energy states that when absorbed may result in thermal energy increases but equally may result in the emission of a photon of that discrete energy.

Thermal energy has a universality based upon the number of atoms in a molecule rather than some configuration of electrons. Again, this universality is witnessed in equations 1 through 6 and 11 through 15. Furthermore, thermal energy concerns broad continuous spectrums, spectrums whose total energy density can be best inferred by heat capacity experiments.

In terms of eq. 22, the energy density of a blackbody spectrum between λ and $d\lambda$ is the energy per mode, times the density of states per photon, times the probability that the mode is occupied. It remains valid as a

mathematical approximation. It is just that the "density of states" must rapidly decrease at the cut-off wavelength for shorter wavelengths (for higher energy photons/phonons), when contemplating thermal energy densities.

Again, the cut-off wavelength is likely not a sharp vertical divide as was graphically depicted herein. It must be acknowledged that the cut-off frequency may vary with states (solids, liquids and gases) as well as with the nature of the matter. Interestingly, some matter's absorption of thermal energy includes visible wavelengths, and the near infrared. These absorptions are primarily due to electrons absorbing energy (as waves), rather than the molecules/atoms themselves. Furthermore, for gases there should be a pressure dependence, which affects the mean free path of the thermal photons.

It is of further interest that one of our estimated cut-off wavelengths ($\lambda_{cut} = 10\ \mu m$) is at the end of what is referred to as the "fingerprint zone" ($2\ \mu m < \lambda < 10\ \mu m$). That being where there are many complex bands that form a molecule's fingerprint. The chosen cut-off also resides in what is often considered as being in the thermal infrared ($8\ \mu m < \lambda < 15\ \mu m$).

This author previously theorized that thermal radiation, e.g., blackbody radiation, may be due to inelastic collisions between atoms and/or molecules. Moreover, it was speculated that the emission of thermal photons was due to collision induced distortions of the electron clouds in both atoms and molecules [4], [12]. Thus, explaining the broad continuous nature of thermal spectrums, at least in the thermal infrared.

Logic implies that if matter radiates thermal photons then that matter should absorb thermal photons. Questions then arise concerning what is the mechanism of absorption? Is it by the electron clouds, or are thermal photons absorbed by another mechanism.

This author has previously discussed that absorption of thermal photons may involve photons behaving as particles thus passing their momentum onto the atoms/molecules [4], [12]. Thus, there may be more to the wave-particle duality of photons than has been accepted.

Whatever the mechanism, thermal equilibrium implies that matter absorbs as much thermal energy as it relinquishes (kinematic plus radiated thermal energy). This is certainly witnessed in enclosures where the walls must absorb as well as radiate thermal photons.

Accordingly, the mechanism of absorption and emission do not

necessarily have to be identical. The only criterion is that when in thermal equilibrium, the total thermal energy in equals the total thermal energy out. Although speculative, one could envision matter absorbing thermal photons as particles and emitting thermal photons due to inelastic collisions, e.g., collision induced distortions of electron clouds.

It should be stated that statistical thermodynamics describes all of a system's energy solely in terms of that system's kinematic energies. Such a description remains a valid approximation for closed systems where the system's total kinematic energy is significantly greater than its total radiative energy [4], [17]. And where the closed system's wall both radiate and absorb thermal photons, thus giving the illusion of elastic collisions [4], [12], [17]-[19].

14. **Conclusions**

We instinctively think in terms of temperature being a measure of warmth, realizing that as the temperature increases, then so too does the thermal energy. Our first experiences involve thermal energy being a linear function of temperature, as is measured in our daily lives using a thermometer. Therefore, when performing thermal energy experiments, one instinctively conforms to it being the matter's heat capacity that varies with temperature. As a powerful mathematical construct, statistical thermodynamics fortified our confidence in what may be erroneous logic.

Contemplating that it is the thermal energy density that varies with temperature, alters our thermodynamic perspective. A perspective that allows heat capacity to be considered as a constant over most temperature regimes. A new perspective that does explain our experimental findings in a simpler context.

Specifically, experiments based upon the thermal energy into (Q_{in}) a system may be better explained in terms of the system's relatively constant heat capacity multiplied by its temperature change (dT). However, the amount of thermal energy required to incrementally increase the temperature (dT) is a not always a linear function of temperature, over all temperature regimes.

There remains a relatively small temperature regime over which the thermal energy required to increase a system's temperature remains a linear function of temperature. That happens to be the temperature regime in which we tend to reside here on Earth's surface, i.e., 250 K < T < 400 K. Seemingly, this reality has skewed our perspective.

Graphs for Planck's blackbody energy density relation were obtained at 25 K intervals for: 50 K < T < 500 K. The total energy density based upon the plots were graphically calculated. Cut-off wavelengths of 8 μm, 10 μm, and 12 μm were then chosen based upon the accepted graph for the heat capacity of mercury, and the graph for the blackbody energy density at: T= 250 K.

All wavelengths longer than the chosen cut-off wavelength were considered to be part of the blackbody's thermal energy. The total blackbody thermal energy density was then graphically calculated, e.g. for a cut-off of: $\lambda_{cut} = 10\ \mu m$, the blackbody spectrum's total thermal energy density was considered to include: $10\mu m < \lambda < \infty$.

Plotting both the blackbody spectrum's total energy density at various temperatures, it became obvious that as expected, the blackbody's total energy density is a rapidly increasing function of temperature.

However, the blackbody spectrum's thermal energy density could be approximated as a linear function of temperature for: 250 K < T < 400 K for all three proposed cut-off wavelengths. Assuming that the blackbody spectrum's thermal energy density must be related to the thermal energy density in matter, gives clarity as to why most of our accepted thermal energy relations are linear increasing functions of temperature.

For temperatures below 250 K the thermal energy density decreases rapidly (e.g., T^4) as the temperature decreases, i.e., as: $T \rightarrow 0\ K$. At absolute zero the thermal energy density is considered to be zero, i.e., all molecular motions cease.

Conversely, for temperatures above 400 K the thermal energy increases more rapidly than a linear relation of temperature would indicate. Unfortunately, the graphical analysis became unsensible for: T > 500 K.

It must be emphasized that this is a preliminary paper, written to show that there is a simpler logic that explains what has been witnessed. The following all warrant more consideration:

- Cut-off wavelengths (e.g.,$\lambda_{cut} = 10\ \mu m$) for thermal energy.
- Nature of thermal energy density for: T > 500 K.
- Relationship between a blackbody spectrum's thermal energy density and thermal energy density in specific matter.

Ultimately, this preliminary analysis separates new thermodynamics from the traditionally accepted theories based strictly upon statistical

thermodynamics, and quantum physics.

Figures

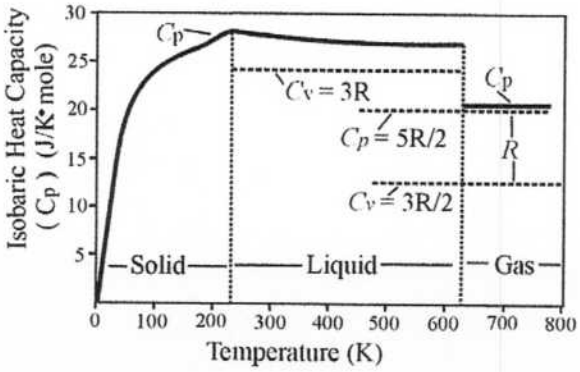

Fig. 1 is a sketch of the heat capacities versus temperature for mercury. Note that discontinuities exist where phase changes occur. Also note that mercury is unreactive, thus when in the gaseous state mercury tends to be a monatomic gas [1].

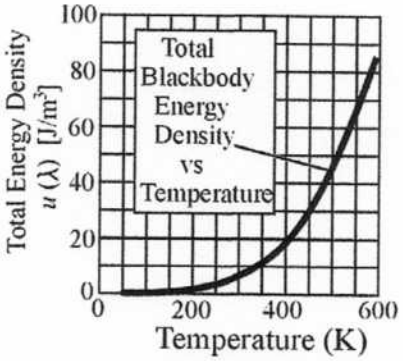

Fig. 2 is a sketch for the total energy density versus temperature, as described by eq. 22.

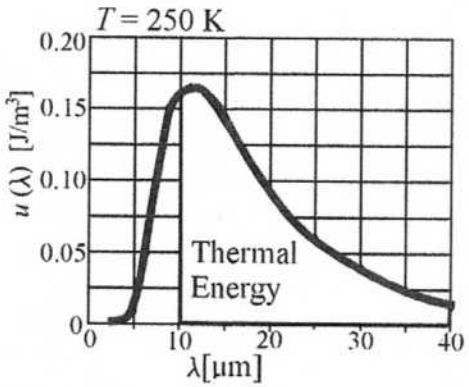

Fig. 3 is a sketch for the blackbody energy density versus wavelength at: $T = 250$ K

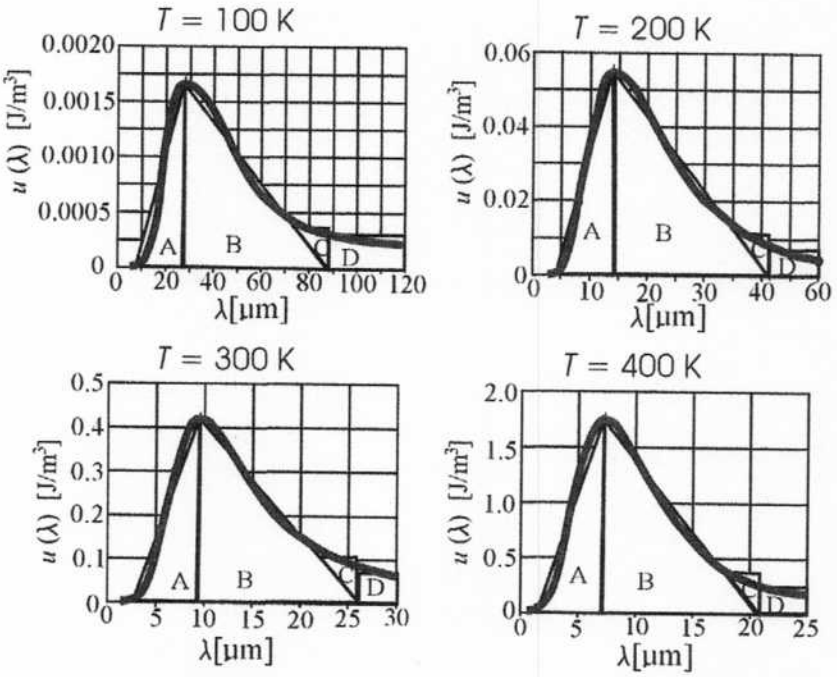

Fig. 4 shows the total energy density versus wavelengths for T=100, T=200, T=300 and T=400. The blackbody energy density is the summation of the areas in triangles A, B and C plus the rectangle D.

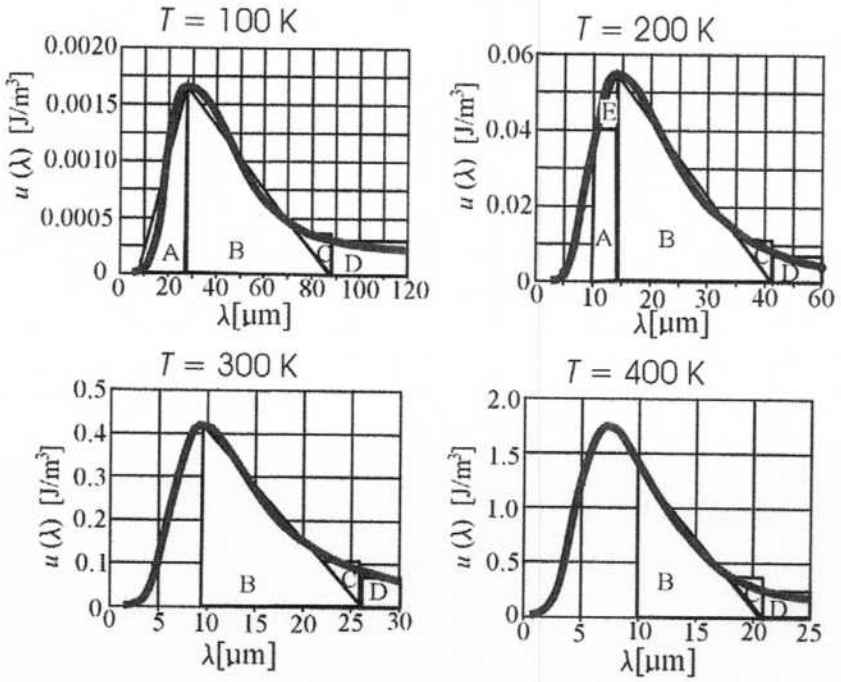

Fig. 5, shows the thermal energy density versus temperature for cut-off: $\lambda = 10\ \mu m$. For: $T = 100$ K it is the summation of: A,B,C & D. For: $T = 200$ K it is the summation of: A,B,C, D & E. For: $T = 300$ K and $T = 400$ K, it is the summation of B,C & D.

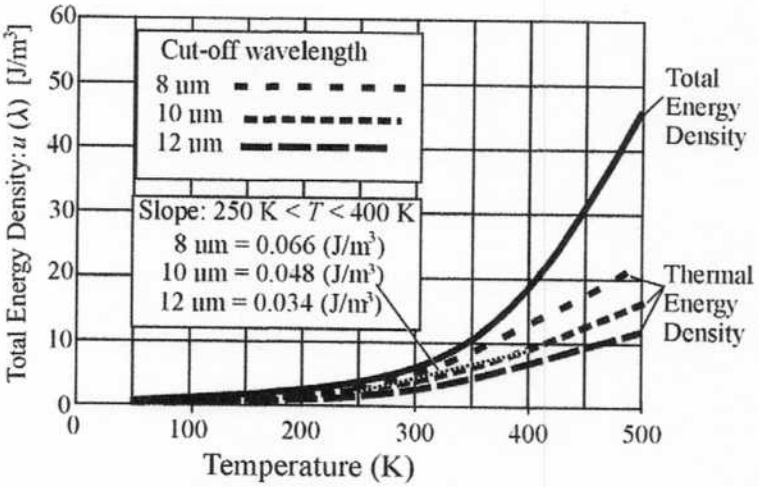

Fig. 6 shows both the total energy density and the thermal energy density versus temperature associated with blackbody radiation for the three chosen

cut-off wavelengths.

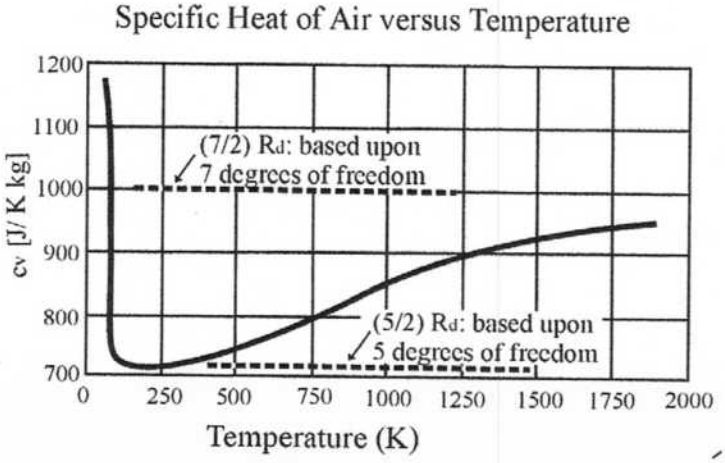

Fig. 7 is a sketch of the specific heat of air versus temperature. Note that: $R_d=RM_d$ that being the dry air constant where M_d is the dry air mass and R is the universal gas constant [14].

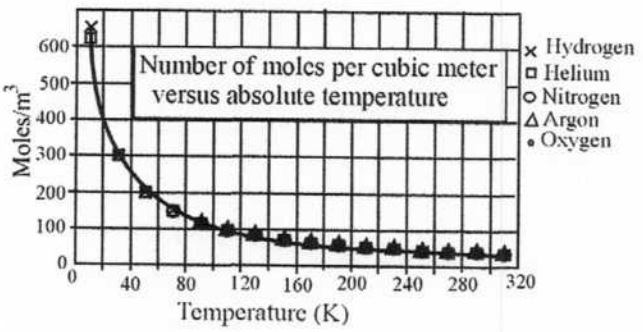

Fig. 8 shows the number of moles per cubic meter of various gases as a function of temperature. Data is in Table 2 at the end of this paper. It is based upon data from the "Handbook of Chemistry and Physics" [15]. Note that this also implies that Avogadro's hypothesis comes into question at low temperatures.

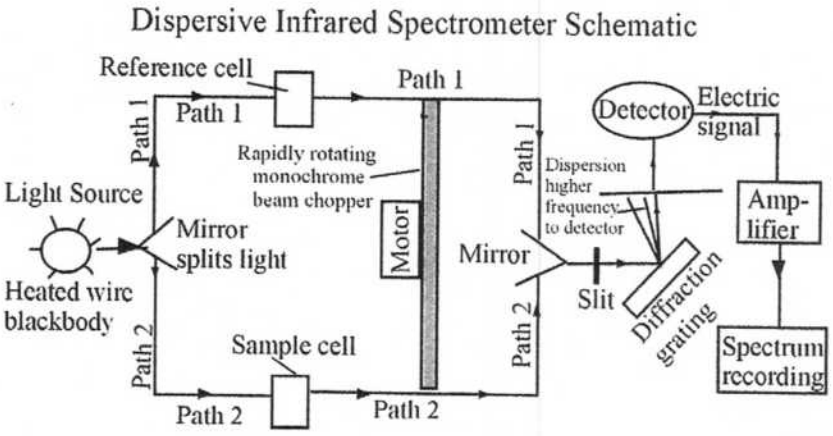

Fig. 9. Is a schematic for a dispersive infrared spectrometer.

Table 1: Gives Blackbody thermal energy at various temperatures

T (K)	Peak λ (um)	Peak $[u(v,T)]$ (J/m^3)	ρ_B Eq.20 (J/m^2)	Total Energy Density (J/m^3)	Thermal Energy Density At three chosen cut-offs (J/m^3)		
					$\lambda = 8\ \mu m$	$\lambda = 10\ \mu m$	$\lambda = 12\ \mu m$
50	60	0.000054	0.354	0.004	0.004	0.004	0.004
75	38.8	0.00041	1.79	0.0214	0.0214	0.0214	0.0214
100	27.5	0.0017	5.67	0.0655	0.065	0.065	0.0644
125	22.9	0.0053	13.8	0.166	0.167	0.166	0.164
150	19.1	0.0133	29	0.347	0.34	0.335	0.328
175	16.7	0.0285	53.2	0.664	0.662	0.643	0.613
200	14.1	0.055	90.7	1.11	1.031	0.971	0.881
225	13	0.1	145.3	1.78	1.74	1.586	1.41
250	11.4	0.167	221.5	2.76	2.59	2.27	1.95
275	10.6	0.27	324.3	3.99	3.58	3.06	2.54
300	9.2	0.42	459.3	5.63	4.72	3.9	3.08
325	8.3	0.625	632.6	7.78	6.1	4.87	3.67
350	8	0.91	850.9	10.53	7.89	6.19	4.69
375	7.5	1.33	1121	13.8	9.99	7.44	5.44
400	7.2	1.77	1452	18.62	12.58	9.45	6.99
425	6.8	2.4	1850	23.17	14.1	10.8	7.75
450	6.4	3.3	2325	30.09	17	12.35	8.85
475	6.1	4.11	2887	38.71	20.57	14.37	10.02
500	5.8	5.2	3544	46.4	23.68	16.48	11.48
525	5.6	6.8	4308	51.95	**	**	**
550	5.3	8.6	5189	68.52	**	**	**
575	5	11	6199	76.53	**	**	**
600	4.7	13.3	7349	84.14	**	**	**
** Non-sensible due to weakness in graphical analysis							

Table 2

	Density at 1 Bar pressure (kg/m^3)					Number of moles per m^3 at 1 Barr pressure				
T (K)	H_2	He	Ar	N_2	O_2	H_2 Atomic mass 2.016	He Atomic mass 4.002	Ar Atomic mass 39.95	N_2 Atomic mass 28.01	O_2 Atomic mass 32.00
0	1.32	2.50				656.25	624.19			
40	0.62	1.20				305.41	299.85			
60	0.41	0.80				201.09	200.05			
80	0.30	0.60		4.38		150.55	150.10		156.31	
100	0.24	0.48	4.92	3.44	3.94	120.78	120.11	123.03	122.69	123.16
120	0.20	0.40	4.06	2.84	3.25	100.20	100.12	101.58	101.38	101.63
140	0.17	0.34	3.46	2.42	2.77	85.86	85.83	86.64	86.53	86.69
160	0.15	0.30	3.02	2.12	2.42	75.10	75.11	75.60	75.53	75.63
180	0.13	0.27	2.68	1.88	2.15	66.77	66.77	67.09	67.04	67.09
200	0.12	0.24	2.41	1.69	1.93	60.07	60.09	60.30	60.26	60.31
220	0.11	0.22	2.19	1.52	1.75	54.61	54.65	54.80	54.40	54.78
240	0.10	0.20	2.01	1.41	1.61	50.10	50.10	50.19	50.15	50.19
260	0.09	0.19	1.85	1.30	1.48	46.58	46.25	46.31	46.30	46.31
280	0.09	0.17	1.72	1.20	1.38	42.93	42.93	42.98	42.98	43.00
300	0.08	0.16	1.60	1.12	1.28	40.06	40.08	40.13	40.09	40.13
320	0.08	0.15	1.50	1.05	1.20	37.56	37.58	37.60	37.59	37.59

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AW signifies Atomic Weight. Note: mols/m^3 calculated by: Density*1000/AW

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